MEMOIRS

OF THE

COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

VOL. III, No. 6

JUNE 1918

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KYOTO

Studies in the Stereochemistry of Quinquevalent Nitrogen. VI.

Configuration of Quinquevalent Nitrogen Compounds.*

By

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(Received Feb. 22, 1918.)

As it is concerned in structural chemistry, the chemical and physical properties of compounds can be explained by the ways of linking of atoms, and also by their numbers in molecule. There are, however, the substances having the same number of atoms and the same ways of linking in molecule, yet exhibiting the different properties. Such phenomena of isomerism can easily be explained in stereochemistry, taking into consideration the spatial arrangements or relative positions of the atoms or atomic groups in molecule.

Le Bel[1] and van't Hoff[2] proposed to explain the existence of optically active carbon compounds based upon the assumption of the asymmetric carbon atom, and Werner[3] is of the opinion that the atoms or atomic gronps in the metal complexes are arranged in space around a metalic atom as centre; in other words the special feature of stereochemistry is not to consider the atoms of equal value in molecule, while it is belived to be the case in structural chemistry.

In stereochemistry, therefore, the chemical and physical properties of compounds should depend principally upon the nature of the central atom. Hence, for the investigation of stereochemistry of nitrogen, the most important factor is to ascertain the nature and directions of its valences.

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* A brief preliminary report was published in the Journal of Tokyo Chemical Society, **36**, 445 (1915).

1 Bull. soc. chi., **22**, 337 (1874).

2 Die Lagerung d. Atome im Raume, 1908, p. 4.

3 Lehrbuch d. Stereochemie, 1904, p. 317; Lieb. Ann. 386, 1 (1912); Ueber d. Konst. u. Confi. Verb. höhre. Ord., 1914.

Proteïnes, vegitable alkaloids and other natural products containing nitrogen in their molecules have not been submitted to chemists as the materials for the stereochemical investigations of the nitrogen atom. Although stereochemistry of carbon compounds was started from the study of the natural product such as betaïnes, choline &c., the quinquevalent nitrogen compounds found in nature have been considered to be unserviceable for the study of stereochemistry of the quinquevalent nitrogen.

Stereochemistry of the quinquevalent nitrogen drew much attention of many chemists[1] at an early date, but our knowledge of it has not yet advanced beyond what is in fact a mere begining of study. The reason may be that we could not find out the natural substances favourable for study, and also have met the difficulty for the preparation of the stable compounds.

Considering of the periodic system of elements, the auther has been led to conceive that the configuration of the quinquevalent nitrogen compounds can be explained on referring the knowledge of the stereochemistry of carbon compounds and metal complexes so for gained.

The first step of study would be to determine whether the five valences of nitrogen in the ammonium compounds are of equal value or not, and the next the investigation of the spatial configuration of the atoms or atomic groups combined with the nitrogen atom, For the solution of the first problem, the existence or non-existence of optically inactive ammonium compounds must be settled. The question on such a subject has been studied by the auther by examining the formation and decomposition of the quarternary ammonium compounds and also their other chemical and physical properties.

In the quarternary ammonium compounds, at least one radical combined with nitrogen is of a negative character, having an electrical nature different from the other four. The quarternary ammonium compounds should be represented by the general formula, NR_4X, X representing the negative atom or atomic group, and their derivatives by the following three types, $NR_3R'X$, $NR_2R'R''X$ and $NRR'R''R'''X$. These compounds are formed by the direct addition of the tertiary

1 H. Jones, Stereochemistry of Nitrogen, 1904; E. Wedekind u. E. Fröhlich, Z. Stereochemie d. funfw. Stickstoff, 1907; E. Wedekind, Die Ent. d. Stereochem. d. funfw. Stick. in letzten Jahrzehnt., 1909.

amines and alkyl derivatives RX (BrCN, O_2, Br_2, CH_3CN, C_2H_5I, $ICH_2CO_2.C_2H_5$&c.) and therefore, there would be several different ways of the formation of the ammonium compounds.

All of the ammonium compounds prepared by different ways were found to be identical by the examination of their melting point, crystalline forms and other physical properties.[1] This seems to stand in favour with the view accepted by a number of chemists about the non-existance of isomer in the inactive ammonium compounds.

With regard to the decomposition[2] of the quarternary ammonium compounds by heat or by electrical means, it may be summarized in the following four types:

1. The ammonium hydroxides and their haloides give the same tertiary amines as seen in methyl allyl phenyl benzyl ammonium compounds:

$$CH_3.C_3H_5.C_6H_5.C_7H_7.N.OH \longrightarrow CH_3.C_3H_5.C_6H_5.N + C_7H_7.OH$$

$$CH_3.C_3H_5.C_6H_5.C_7H_7.NI \longrightarrow CH_3.C_3H_5.C_6H_5.N + C_7H_7.I$$

2. The ammonium hydroxides and their haloides give different tertiary amines; for example, trimethyl ethyl ammonium hydroxide is decomposed into trimethyl amine and ethyl alcohol but its iodide into dimethyl ethyl amine and methyl iodide;

$$(CH_3)_3.C_2H_5.NI \begin{cases} \nearrow (CH_3)_3.C_2H_5.N.OH \longrightarrow (CH_3)_3.N + C_2H_5.OH \\ \searrow (CH_3)_2.C_2H_5.N + CH_3I \end{cases}$$

3. As we have seen in the case of dimethyl phenyl ethyl acetate ammonium iodide, the double dissociation of molecule takes place as the following scheme shows:

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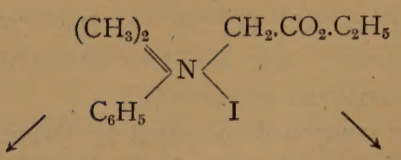
1 Wedekind, Die Ent. d. Stereochem. d. funfw. Stick. in letzten Jahrzehnt., 1909; Wedekind u. Fröhlich, Z. Stereochem. d. funfw. Stick., 1907, p. 68.; Wedekind, Ber. D. chem. Ges., **34**, 3991 (1901); **35**, 183, 3580 (1902); **36**, 1158, 3791 (1903); **37**, 2712, 3894 (1904); Jones, J. Chem. Soc., **85**, 224 (1904); Kipping, Ibid., **83**, 874, 889, 902, 1147 (1903); **87**, 628 (1905); Collie and Schryver, Chem. News, **63**, 174 (1891); Komatsu, Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912).

2 Braun, Lieb. Ann. **382**, 1 (1911); **386**, 273 (1912); Singh, J. Chem., Soc., **109**, 780 (1916); Komatsu, Mem. Coll. Sci. Engin., Kyoto, **3**, 371 (1912); Mem. Coll. Sci, Kyoto, **1**, 370 (1916); Wedekind, Ber. D. chem. Ges., **35**, 766, 1075 (1902); Dunlop, J. Chem. Soc., **101**, 1999 (1912); Emde, Arch. Pharm., **249**, 106, 111, 118 (1911); **247**, 369 (1909); Ber D. chem. Ges., **42**, 2590 (1909); Sidgwick, Organic Chemistry of nitrogen. 1919. p.23.



$$ICH_2.CO_2.C_2H_5 + (CH_3)_2C_6H_5.N \begin{matrix} CH_3 \\ C_6H_5 \end{matrix} > N.CH_2.CO_2.C_2H_5 + CH_3I$$

4. By heating or by electrolysis, methyl ethyl propyl phenyl ammonium hydroxide is decomposed into methyl ethyl aniline or methyl ethyl propyl amine respectively:

$$\left.\begin{matrix} CH_3.C_2H_5.C_6H_5.N + C_3H_7I \\ CH_3.C_3H_7.C_6H_5.N + C_2H_5I \\ C_2H_5.C_3H_7.C_6H_5.N + CH_3I \end{matrix}\right\} \longrightarrow CH_3.C_2H_5.C_3H_7.C_6H_5.N.I \longrightarrow$$

$$CH_3.C_2H_5.C_3H_7.C_6H_5.N.OH \begin{matrix} \xrightarrow{\text{heating}} CH_3.C_2H_5.C_6H_5.N + C_3H_7.OH \\ \xrightarrow{\text{electrolysis}} CH_3.C_2H_5.C_3H_7.N + C_6H_6 \end{matrix}$$

Decomposition of the quarternary ammonium compounds being so complex that we can not give a general rule, but throughout all the cases the auther has noticed that one and the same ammonium compound prepared from different sources yields the identical tertiary amine by the same treatment. Now it is highly probable that nature of decomposition of the compounds depends upon the mutual influence of the electrical character of the alkyl groups linked to nitrogen, but not upon their relative positions in the molecule, like the double decomposition and substitution in the metal complexes.[1] Such a fact naturally leads us to the hypothesis that the four negative valences of the quinquevalent nitrogen are of the same value. Through the investigations of Meisenheimer and his co-workers[2] and of the author[3] on the derivatives of the types $(R_3)N<\begin{matrix}OR\\OH\end{matrix}$ and $(R)_3N<\begin{matrix}OH\\OR\end{matrix}$ from trialkyl amine oxide $(R)_3N{:}O$, there may be drawn a conclusion that the nature of the fifth valence of the nitrogen atom is entirely different from that of four negative velences. For the confirmation of the

1 Werner, Lieb. Ann., **386**, 1 (1912).

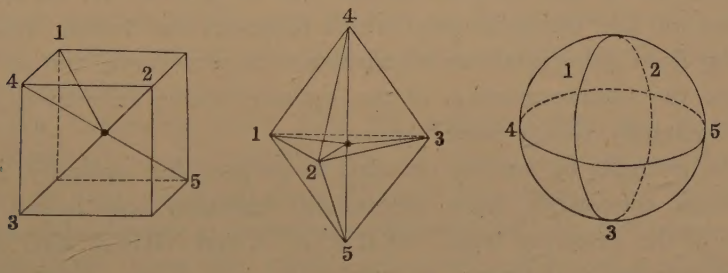
2 Ibid., **385**. 13, 117 (1912); **397**, 273 (1913); Ber. D. chem. Ges., **41**, 3966 (1909)

3 Mem. Coll. Sci., Kyoto, **1**, 316 (1916).

above view, the auther[1] has also studied the absorption spectra of the quarternary ammonium compounds. The absorption spectra of the ultra violet rays of the quarternary ammonium compounds are independent of the nature of the atom or atomic group (excepting the atomic group which itself has the absorption spectra) combined by the negative valence to the nitrogen, but depends upon that of the atoms or atomic groups combined by the negative valences of nitrogen.

Now, we have to discuss the second problem, i.e., the direction of the valences of the quinquevalent nitrogen or the spatial configuration of the quarternary ammonium compounds. Thus, the different views brought forward by the different investigators, will be stated below:

Fig. I. Fig. II. Fig. III.



1. Van't Hoff[2] suggested the cubic configuration, supposing the nitrogen atom to be situated at the centre of a cube, and the five atoms or atomic groups at the five solid angles as shown in Fig. I.

2. Willgerodt[3] proposed the double tetrahedron configuration, modifying van't Hoff's view, as shown in Fig. II.

3. Fröhlich,[4] from his study in the autoracemisation of an optically active ammonium compound in solution, has been induced to the notion that the configuration of ammonium compounds would be represented by a sphere as shown in Fig. III, in which the nitrogen atom is situated at the centre and the five atomic groups on the great circles at right angles to each other.

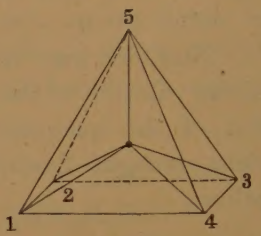
All those configurations founded on the same principle possess

1 Mem. Coll. Sci., Kyoto, **1**, 303 (1916).
2 Ansichten u. Org. chem., 1878, p. 80.
3 J. prak. Chem., **41**, 291 (1890).
4 Z. Stereochem. d. funfw. Stick., 1907. p. 43.

the same defects and merits, so that none of them can explaine the non-equivalenee of the five valences of quinquevalent nitrogen or the non-existence of the isomerides of the inactive ammonium compounds.

4. The pyramidal configuration by Bischoff[1] represented by Fig. IV. and based upon Jone's[2] assumption on the mode of formation of ammonium compounds from amines stands in harmony with the decomposition and formation of the ammonium compounds, but not with their absorption spectra of the ultra violet rays and with the asymmetry of the molecule.

Fig. IV.



It is quite strange that we have not yet observed the existence of an optically active ammonium compound in nature; this may be ascribed to the specific character of the nitrogen atom which possesses no definite valency, changing from quinquevalence to trivalence or vice versa, and as consequence the autoracemisation of the optically active ammonium compounds naturally taking place.[3]

The attempts by various chemists to prepare the optically active ammonium compounds were successfully executed only in the compounds of the following types, NRR′R″R‴X and NRR′R″XX. They may be grouped as follows:

1. Methyl ethyl propyl isobutyl ammonium chloride,[4]
   $CH_3.C_2H_5.C_3H_7.C_4H_9.NCl$
2. Methyl allyl phenyl benzyl ammonium iodide[5]
   $CH_3.C_3H_5.C_6H_5.C_7H_7.NI$
3. Methyl allyl tetrahydroisoquinolium iodide,[6]

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1 Ber. D. chem. Ges., **23**, 1972 (1890).

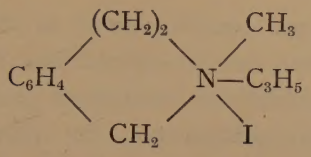
2 J. Chem. Soc., **87**, 1730 (1905)

3 Komatsu, Mem. Coll. Sci., Kyoto, **1**, 231 (1915); Pope and Harvey, J. Chem. Soc., **91**, 828 (1901).

4 Le Bel, Compt. rend., **112**, 724 (1891); **129**, 549 (1899).

5 Pope and Peachey. J. chem. Soc., **75**, 1127 (1899); **79**, 828 (1901); **101**, 519 (1912); Wedekind, Ber. D. chem. Ges., **32**, 722 (1899); **38**, 438 (1905); Z. phys. Chem., **45**, 235, (1903); Jones, J. Chem. Soc., **83**, 1418 (1903); **85**, 223 (1904); **87**, 1721 (1905); **89**, 280 (1906); **93**, 1790 (1908); Komotsu, Mem. Coll. Sci., Kyoto, **1**, 123 (1915); Wedekind und Fröhlich, Stereochem., 1907, p. 36; Reilly, J. Chem. Soc., **111**, 21 (1917).

6 Wedekind., Ber. D. chem. Ges., **32**, 722 (1899); **38**, 1642 (1905); **40**, 4450 (1997); **41**, 456 (1908); **42**, 2138 (109); **45**, 1293 (1912);



4. Methyl ethyl phenyl hydrazonium iodide,[1]

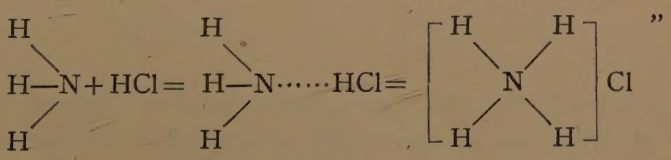
$CH_3.C_2H_5.C_6H_5.NH_2.NI.$

5. Methyl ethyl aniline oxide[3] or Methyl ethyl phenyl ammonium oxide,

$CH_3.C_2H_5.C_6H_5.N:O$ or $CH_3.C_2H_5.C_6H_5.N(OH)_2$

The existence of each of these compounds in the optical antipodes not only suggests the non-equivalence of five valences of the nitrogen atom, but also gives us an assurance that the asymmetry of the molecule depends wholly upon the four groups attached to the nitrogen by the positive valence, the fifth so-called negative group exerting no influence whatever on it.

For explaining these facts Meisenheimer[2] has put forward an hypothesis about the configuralion of ammonium compounds which seems to have originated from Werner's hypothesis.[3] He states "Das Ammoniak bindet zunächst den Wasserstoff der Salzsaure durch Nebenvalenz. Dan tritt Affinitätsausgleich ein, so daß schließlich alle vier Wasserstoffatome durch gleiche Affinitäts beträge, die aber geringer sind als eine volle Affinität, an den Stickstoff gebunden sind....." 'An den einzelnen Atomen des Komplexes NH_4 sind noch bestimmte Affinitätsbeträge ungesättigt, die das Radikal NH_4 nach außen hinzer Wirkung bringt, wodurch es Einwertig wird' "und so also den Säurerest bindet:



With regard to the configuration of ammonium compounds, he further states" Sämtliche funf Radikale sind durch Hauptvalenz an

1 Singh, J. Chem. Soc., **103**, 604 (1913); **105**, 1972 (1914).
2 Meisenheimer, Ber. D. chem. Ges, **48**, 396 (1908); Lieb. Ann., **385**, 117 (1911).
3 Lieb. Ann., **397**, 280 (1913).
4 Lehrbuch d. Stereocehmie, 1904, p. 310.

den Stickstoff gebunden, vier in einer inneren, eines in der äußeren Zone..... Der in der außenzone stehende ebenfalls durch Hauptvalenz gebundene Säurerest nimmt, wie in tautomeren Substanzen—wenigstens in Lösung—keine festen platzen und hat daher auf die Asymmetrie des Moleküle keine Einfluß."

Ammonium compounds with regard to their molecular asymmetry should bear close analogy to carbon compounds,[1] and comparing their absorption spectra, formation and other reactions with those of metal complexes,[2] one can not fail to admit that there is a great similarity. Hence, the auther is of the same opinion with Werner and Meisenheimer in some respects with regard to the configuration of ammonium compounds.

The auther's conception for the configuration of quarternary ammonium componnds is that the coordinate number of nitrogen is four, and the four atoms or atomic groups in the inner zone is supposed to be situated at four corners of a tetrahedron or on the surface of a sphere, i.e., the nitrogen atom is at the centre of a tetrahedron or sphere, and the four groups at its four corners.

The negative atom or atomic group in the outer zone is attached to the nitrogen in one definite position as shown in Figs. V and VI.

Fig. V.

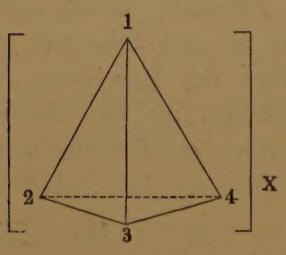
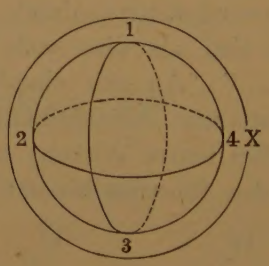


Fig. VI.



Its position in the outer zone may, therefore, depend upon the manner of formation of ammonium compounds and exerts an in-

1 Wedekind, Ber. D. chem. Ges., **36.** 1163, 3800 (1903); **38,** 1843 (1905); **42,** 303 (1909); Lieb. Ann. **401,** 326; **404,** 322 (1914); Scholtz, Ber. D. chem, Ges., **37,** 3627 (1904); **38,** 595, 1289 (1905); **40,** 685 (1907); Jones, J. Chem. Soc., **87,** 135 (1905); Aschan., Z. phys. Chem., **46,** 304 (1903); Mills and Bain, J. Chem. Soc., **105,** 64 (1914).

2 Werner. Lieb. Ann., 386, 1 (1912); Nicoloplos, Z. phys. Chem., **82,** 361 (1913); Shibata, J. Coll. Sci., Tokyo, **37,** 1 (1915); Compt. rend., **157,** 593. (1913); Komatsu, Mem. Coll. Sci., Kyoto. **1,** 303 (1916).

fluence upon the rotation of the compounds, but not upon the decomposition and other chemical and physical properties.

According to Werner and Meisenheimer's view for the configuration, the atom or atomic group in the outer zone would exert no influence upon the asymmetry of molecule, so that there exists no isomers of the different rotatory powers in the same ammonium compound. The auther has, however, succeded in isolating α and γ active forms in methyl allyl phenyl benzyl ammonium compound[1]. By autoracemisation α form was found to convert to the stable γ form[2]; so the auther's opinion has now been definitely comfirmed.

Applying the auther's hypothesis to solution, it is evident that when the molecule AB dissociates into A and B there may still exist a kind of chemical affinity between them,[3] being supposed to be different from the Arrhenius electrolytic dissociation:

$$AB \rightleftarrows A^+ + B^-$$

and so called dissociation degree is assumed to be dependent upon the strength of affinity between two particles or distance between them. Now the facts that the ratatory power of the ammonium salts of optically active acids[4], being of a specific nature, has neither additive nor ionic properties well coincide with the auther's view.

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1 Komatsu, Mem. Coll. Sci., Kyoto **1**, 123 (1915).

2 Ibid., **1**, 231 (1915).

3 Ibid., **1**, 234 (1915).

4 Van't Hoff, Die Lagerung d. Atome im Raume. 1908, p. 75–92.

Lithium Spectrum in an Electric Field.

By

Usaburo Yoshida.

(Received Feb. 23, 1918.)

After an investigation of the effect of an electric field on the spectrum lines of lithium had been made by Stark[1], Howell[2] attacked the problem by the method first employed by Lo Surdo.[3] Their results were in agreement; but, as they were confined to a certain definite electric field, the relation between the displacements of the components of the lithium lines and the intensity of the electric field was not clearly brought out. In the course of the investigations carried out by T. Takamine and the writer[4], it was shown that Lo Surdo's method was adapted to a study of this relation; and, therefore, in the present investigation, Lo Surdo's method was again employed.

Experimental Arrangement.

A photographic arrangement essentially as described in one of the papers by T. Takamine and the writer[5] was employed. Four-prism-spectrograph for the line λ 4602, and a three-prism-spectrograph for the lines λ 4132 and λ 4148 were used.

For obtaining the spectrum, the vacuum tube shown in Fig. 1 was taken. A glass bulb, in volume about 2 litres, had four side tubes. A glass tube E, containing the cathode, was inserted in the side tube A, and the anode was sealed in the side tube B. At the end of the side tube C, whose diameter was about 3 cms, a plane parallel glass plate was attached by means of sealing wax, so that a

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1 Elektrische Spekralanalyse chemischer Atome, (1914).

2 Astrophys. J., **44**, 87, (1916).

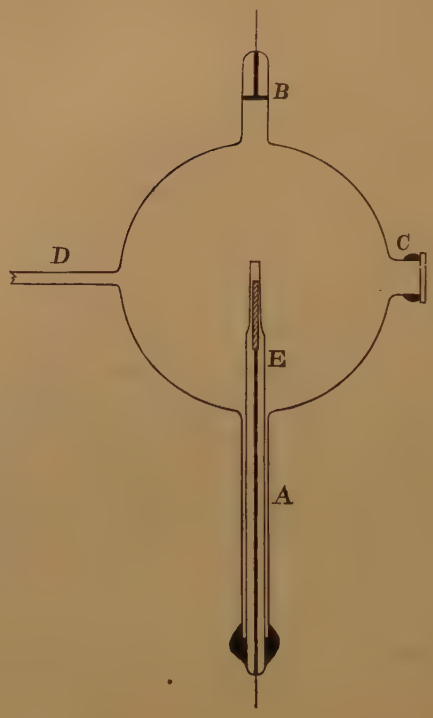
3 Rendiconti d. Lincei, **22**, 664, (1913).

4 Mem. Coll. Sci., Kyoto, **2**, 137, 321, 325, (1917).

5 Mem. Coll. Sci., Kyoto, **2**, 137, (1917).

fine image of the luminous glow in the Crookes dark space could be projected on the slit of the spectrograph by means of a projection-lens. For this a Cooke's chinematographic lens of two inches focal length was used. Lastly, the side tube D served to connect the bulb to a Gaede pump. The upper portion of the tube E, in which the cathode was inserted, was a capillary tube. Many capillary tubes of various diameters ranging from 2 mm. to 4 mm. were used. In the side of the capillary tube just opposite to the plane parallel plate window and at the upper part, a slit of about 1 mm. wide and 6 mm. long was cut parallel to the axis of the tube. This slit extended down to the level of the top surface of the cathode. This form of tube was first employed by J. A. Anderson.[1]

Fig. 1.



In order to obtain the lithium spectrum, metallic lithium was used as the cathode. Sometimes it was attached to an aluminium rod, and sometimes deposited at the end of an aluminium rod by electrolysis. The lithium-cathode thus prepared was of such a size that it completely filled the upper capillary portion of the tube E. When the top surface of the lithium-cathode was a very little below the level of the lower end of the slit, the end of the Crookes' dark space, whose length was in most cases of the order of the diameter

1 Astrophys. J., 46, 104, (1917).

of the capillary tube, was well marked, and comparatively fine components of hydrogen and lithium spectra were obtained.

For the excitation of the discharge in the vacuum tube, an induction coil whose maximum spark-length was 15 cms. was employed. The current in the secondary circuit of the coil was rectified by a valve tube and a spark gap connected in series. The mean current thus rectified was of various intensities, ranging from 0.5 m.A. to 1 m.A.

The intensity of the lithium spectrum was much stronger when air was used as residual gas than when hydrogen was employed, as was observed by J. A. Anderson[1] in the case of some other metals. For this reason, the writer used air as residual gas. The hydrogen lines which were needed for the determination of the electric field were always evidenced with a tolerable intensity by the presence of moisture.

Results.

The spectrum lines of lithium examined in the present experiment were λ6103.8, λ4602.4, λ4132.4 and λ4148.2. Among these, λ6103.8 sufferred no marked influence in the electric field whose intensity was estimated to be about 30000 volt per centimeter. This result agrees well with that of Stark who states that the effect was small in the electric field of 38000 volts per centimeter.

λ4602.4. With a four-prism-spectrograph, the dispersion at this line was 11.1 Å.U. per mm. on the photographic plate. As the intensities of the parallel components were much more reduced than those of the perpendicular components, it was difficult to obtain a good impression fit for the measurement of both components on the same photographic plate. Consequently, the writer was compelled to measure the components separately on different plates. The photograph reproduced in Fig. 2, Plate 1, was used for the perpendicular components, that in Fig. 3, Plate 1, for the parallel components. For the determination of the field-strength, the separation of $H\beta$ was used, because, for this line, the proportionality between the separation and the field-strength had been established by Stark and Kirschbaum, and Wilsar on the parallel and perpendicular components respectively. For the separations of this β line the values 3.0 Å.U. per 10000 volts/cm. for p-components, and 1.4 Å.U. per 10000 volt/cm. for

1 Astrophys. J. **46**, 104, (1917).

s-components, given by Stark, were employed. The results of measurements are tabulated in Table 1, and the curve drawn in Fig. 5, Plate II, represents the manner of decomposition of the line λ 4602 in several electric fields. The mark ✻S represents the value observed by Stark, and the mark ✻H that by Howell.

Table 1, λ 4602.

p-component.

E in 10^4 volt/cm	2·40	2·13	1·89	1·56	1·44	1·24	1·02	0·85	0·65	0·46
displacement of the v-comp. in Å.U.	−2·9	−2·6	−2·5	−2·3	−2·1	−1·7	−1·5	−1·3	−1·1	−1·1
displacement of the r-comp. in Å.U.	+1·4	+1·3	+1·1	+1·0	+0·8	+0·8	+0·7	+0·6	+0·4	+0·3

s-component.

E in 10^4 volt/cm	3·61	2·87	2·48	1·78	1·28	0·82				
displacement of the v-comp. in Å.U.	−3·1	−2·7	−2·4	−2·1	−1·8	−1·5				
displacement of the r-comp. in Å.U.	+1·5	+1·3	+1·1	+0·7	+0·6	+0·4				

In the present experiment, only two components were observed both in the parallel and perpendicular components respectively. The component which corresponds to the central one observed by Stark did not make its appearance. It is not, of course, clearly decided by the present experiment whether or not there is a very weak central component. With regard to the existence of this central component, Stark also was in doubt. Further study is needed to decide this point.

As the undisplaced component did not really appear in the photograph, the position of this line was determined indirectly. Measuring the distance between the two unaffected spectrum lines which were in the neighbourhood of the line λ 4602, it was seen that the distance was the same at different hights along the lines. One of these lines was taken as a reference-line, and the distance between this line and the line λ 4602 was measured in the region where no electric effect

was observed. From this distance the undisplaced position of the line $\lambda 4602$ was determined in the electric field. Such a method of determining the undisplaced position of an affected line was applied to the case of $\lambda 4132$ and $\lambda 4148.2$ also.

As is clearly seen from the curve, the displacement of the red component is proportional to the electric field both in the parallel and perpendicular component. With regard to the violet component-line, although the linear relation between its displacement and the electric force is established, yet its continuation does not pass through the origin. Moreover, the intensity of this component decreases more rapidly than that of the red component, as we pass from a stronger part of electric field to a weaker one, and at last vanishes in a field weaker than about 5000 volt per centimeter. As it is highly important to decide whether or not this component is really an isolated one of the line the writer made further minute examination. Making the condition of excitation nearly equal, three photographs were taken; first with an exposure of 40 minutes, the second with an exposure of two hours and a half, and the third with an exposure of six hours and a half. In all these photographs, the violet component made its appearance up to the field of about 5000 volt per centimeter, and no trace of its continuation was detected in the weaker field. Of course, this phenomenon was observed especially on the perpendicular component. Judging from this, it seems natural to consider that the violet component appears in an electric field stronger than 5000 volt per centimeter. The mark ⊙ drawn at the upper ends of the violet components represents roughly this critical electric field.

Generally speaking, the separation of the parallel components is somewhat greater than that of the perpendicular ones. And the displacement of the violet components is greater than that of the red ones. These facts agree well with the results obtained by Stark and Howell. But with regard to the amount of displacements of the components, the values obtained by Stark are smaller than that got by the present writer. As the intensity of the components was increased, the image of the components appeared much broadened; and consequently, the measurement was made from plates on which the image of the component appeared comparatively weak but sharp.

The spectrum line $\lambda 4602$ is of special interest. Kayser[1] regards

1 Handbuch d. Spektroskopie, Vol. II, p. 366.

this as a line easily reversed and much broadened toward the red side. Saunders[1] examined it more closely. He took a set of several photographs of this line on a film, varying exposures and amounts of vapor in the arc so as to furnish wide differences among the set. From the constancy of the distance between the points of maximum density in the image on either side of the "reversal", he concluded that this image, which was considered by Kayser as due to "reversal", is due to the presence of two neighboring lines; namely, a stronger one at λ 4603.2 much broadened toward the red, and a weaker one at λ 4601.6 broadened toward the violet side.

With regard to the broadening of a spectrum line in virtue of a great vapour or current density, Stark[2] considered that it might be accounted for as the effect of an electric field, due to the neighbouring molecules or atoms, on the spectrum lines emitted by the source. In fact the correspondency between the broadening of spectrum lines and their behavior in an electric field was found by Stark and Kirschbaum,[3] and Wendt[4] to hold good of the spectrum lines of certain elements examined. Especially on the spectrum lines of Li, similarity of the two phenomena was noted by Stark and Kirschbaum.

Now, returning to our problem, the fact that the line λ 4602 is a double line seems to be accounted for by the view mentioned above. The facts that the violet component is isolated and that the distance between the violet and the red components is always greater than ca. 1 Å.U. both in the parallel and the perpendicular component, agree well with Saunders' results that the line λ 4602 is double and the distance between the two lines is 1.6 Å.U. Again the intensity of the violet component is weaker than that of the red one both in the parallel and perpendicular component. This assymmetry of the intensities of the two components was also noted by Saunders in the case of the double lines of λ 4602. Lastly the fact observed by Saunders that both of the double line were diffused toward the outer sides seems to be accounted for by the fact that the displacements of both the components observed in the present experiment increased more and more on both sides respectively as the field-strength was increased.

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1 Astrophys. J., **20**, 188, (1904).

2 Elektrische Spektralanalyse chemischer Atome, (1914).

3 Ibid.

4 Ibid.

λ 4132. With a three-prism-spectrograph, the dispersion at this line was 29.5 Å.U. per mm. on the photographic plate. The photograph reproduced in Fig. 4, Plate I, represents the manner of decomposition of this line in a heterogeneous electric field. For the determination of the electric field, the separations of H_γ and H_δ were used. Using Stark's data, the field strength calculated from the separations of these two lines was found to agree fairly well, and consequently the mean value of these two were employed.

The numerical data obtained are tabulated in Table 2, and graphically represented in Fig. 6, Plate II.

Table 2, λ 4132.

p-component.

E in 10^4 volt/cm.	3·37	2·78	2·21	1·78	1·38	0·99		
δλ of the v-comp. in Å.U.	−5·4	−4·1	−3·5	−2·9	−2·0	−1·4		
δλ of the middle comp. in Å.U.	−0·5	−0·3	−0·2	−0·2	−0·1	−0·1		
δλ of the r-comp. in Å.U.	+4·5	+3·8	+3·2	+2·8	+1·9	+1·4		

s-component.

E in 10^4 volt/cm.	3·76	3·19	2·55	2·09	1·84	1·54	1·24	1·13
δλ of the v-comp. in Å.U.	−5·0	−4·0	−3·3	−2·6	−2·2	−2·2	−1·7	−1·3
δλ of the middle comp. in Å.U.	−0·3	−0·2	0	0	0	0	0	0
δλ of the r-comp. in Å.U.	+4·5	+3·9	+3·2	+2·6	+2·1	+1·9	+1·7	+1·3

Both in the parallel and the perpendicular components, three components were obtained respectively. Generally speaking, the behavior of the perpendicular components is similar to that of the parallel ones. The only difference is that the displacements of the former are some-

what slighter than those of the latter. The displacements of the outer two components are proportional to the field-strength, the displacement of the violet component being a little slighter than that of the other. The slight displacement of the central component is toward the violet side. These facts were of course ascertained in the parallel and the perpendicular components respectively. As to the amount of separation, the values observed in the present experiment were somewhat different from those obtained by Stark, but they agreed fairly well with those of Howell.

λ 4148.2 This line was first discovered by Konen and Hagenbach,[1] confirmed by Saunders,[2] and is a member of a combination series of lithium. They observed many spectrum lines belonging to this series in an arc; and found all weak in comparison with the lines belonging to the other series. All were diffused toward the red side.

In the present experiment, a weak line in the neighbourhood of λ 4147 was found to displace toward the red when the field strength was increased. The result of measurement is given in Table 3, and graphically represented in Fig. 7, Plate II.

Table 3, λ 4148.2

p-component.

E in 10^4 volt/cm.	3·37	2·78	2·21
in Å.U.	4147·9	4147·9	4147·1

s-component.

E in 10^4 volt/cm.	3·76	3·19	2·55
λ in Å.U.	4148·0	4147·5	4147·0

Here it must be noted that the maximum error in determining the wave length was about 0.5 Å.U. As the line appeared only when a

1 Phys. Z.S., **4**, 801, (1902–1903).
2 Astrophys. J., **20**, 188, (1904).

lithium-cathode was used under various experimental conditions, this may be ascribed to lithium. Moreover, when a lithium cathode was used, a trace of a weak line appeared at λ4636, which might probably be a member of the same series. If so, the line at λ4147 might be considered as the same line found by Konen and Hagenbach at 4149.1 Å.U., and by Saunders at 4148.2 Å.U.

The intensity of this line diminished as the field-strength was decreased, and at last vanished in a field weaker than about 15000 volt per centimeter.

The wave length of the line increased linearly with the field-strength, both in the parallel and the perpendicular component, and surpassed 4148 Å.U. at 40000 volt per centimeter. Taking into consideration the explanation of the broadening of a spectral line given by Stark, the fact that this line appears diffused toward the red seems to be easily accounted for by the behavior of this line in an electric field.

Comparison with those of He. Corresponding lines of the diffuse series of He and Li are represented in Table 4.

Table 4.

Corresponding lines of the diffuse series of He and Li

Term number	2	3	4	5
He	5875·9	4471·7	4026·3	3819·8
Li	6103·8	4602·4	4132·4	3915·4

Similar behavior of the corresponding lines of these two elements in an electric field was noticed by Stark. In addition to the similarity mentioned by Stark, we may here add certain new points observed later. Of the line λ4472 of He, Stark observed 3 p- and 3 s-components, of which the central ones are marked questionable. By further investigation, carried out by T. Takamine and the writer[1], 7 p- and 5 s-components were obtained, of which the central ones are, of course, questionable, as the rectification of the secondary current of the induction coil might not have been perfect.

1 Mem. Coll. Sci., Kyoto, **2**, 325, (1917).

In the case of λ 4602 of lithium, only two p- and two s-components have been hitherto clearly observed, and so many components as in the case of λ 4472 of He have not been obtained. Whether both p- and s-components of λ 4602 decompose themselves into others or not can be decided only by future investigation; but, so far as the "Grobzerlegung" is concerned, the number of components of λ 4472 may be said to be two both in p- and s-components respectively. In a former investigation on He, it was stated that the three violet components of λ 4472 were isolated both on p- and s-components. Considering this from the standpoint of "Grobzerlegung", we may say that both p- and s-components of λ 4472 have one isolated violet component respectively. The same phenomenon was observed in the case of λ 4602 of lithium, as was stated before.

For the line λ 4026 of He, Stark observed 3 p- and 3 s-components. T. Takamine and N. Kokubu[1] give 5 p- and 5 s-components. But, from the standpoint of "Grobzerlegung", it may be considered as 3 p- and 3 s-components, of which the central ones displace a little toward the violet, both in parallel and perpendicular components respectively. T. Takamine and N. Kokubu also noticed that the violet two components were isolated both in the parallel and perpendicular components, but they remarked that the appearance of the isolated components was not well defined. Moreover the displacements of the violet p- and s-components of this line seems to increase nearly proportional to the field-strength. Considering these facts, we may say that the isolation of the two violet p- and s-components of 4026 is not definitely proven.

In the case of λ 4132 of lithium, two outer p- and s-components whose displacements were proportional to the field-strength, and a central p- and s-component which displaced a little toward the violet, were found. But no trace of the isolation of the components of this line was detected in the present experiment. Disregarding the somewhat ambiguous isolation of the violet components of λ 4026 of He, λ 4132 of lithium seems to decompose similarly, so far as "Grobzerlegung" is concerned, as λ 4026 of helium, which corresponds to λ 4132 of lithium.

Isolated components. Many isolated components have been hitherto observed on the spectrum lines of He, Ne, and Li by T. Takamine

1 Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

and the writer,[1] Nyquist,[2] T. Takamine and N. Kokubu[3] and the writer. As all these isolated components appeared similarly on the violet sides of the original lines in their immediate neighbourhood, the view naturally arises that they may be due to a similar cause.

The present investigation on the isolated component of 4602 of lithium shows that no plolongation of this component into the region of smaller field-strength occurs, however the intensity of the line be increased. Taking these facts into consideration, it seems natural to consider that electronic vibration corresponding to an isolated component becomes possible in a given electric field, and thence this electric vibration increases in intensity as the electric field is increased.

Lastly, concerning the relation between an isolated component and the original spectrum line, Nyquist states that they are closely related, and that it is perhaps best to treat the former as a component of the latter. Considering the fact that all isolated components hitherto found appeared similarly on the violet sides of the original spectrum lines, in their immediate neighbourhood, the suggestion given by Nyquist seems to be probable.

Summary.

1. The effect of an electric field on certain spectrum lines of lithium has been studied by Lo Surdo's method.

2. The peculiarity of lines 4602 and 4148.2 in an arc has been explained as the effect of an electric field on these lines.

3. Certain similarity between the corresponding lines of He and Li has been mentioned.

In conclusion, the writer's sincere thanks are due to Profs. T. Mizuno and M. Kimura for the interest they have taken in the research. The writer's thanks are also due to Prof. M. Fukui of Kyoto Higher Technical School for the loan of a Krüss spectrometer.

1 Mem. Coll. Sci., Kyoto, **2**, 325, (1917).

2 Phys. R., **10**. 226, (1917).

3 Mem. Coll. Sci., Kyoto, **3**, 81, (1918).

Fig. 2.

Magnification : 5

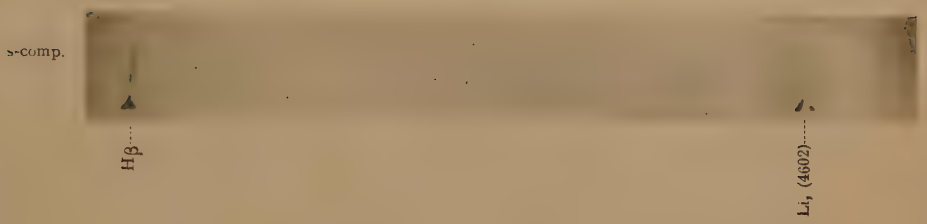


Fig. 3.

Magnification : 4·8

Fig. 4

Magnification : 7·1

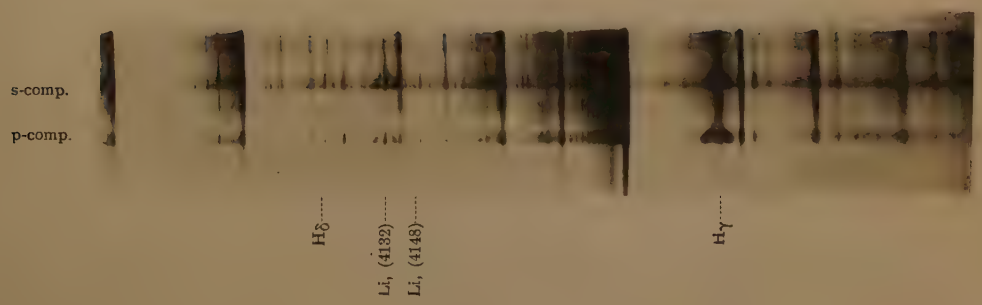
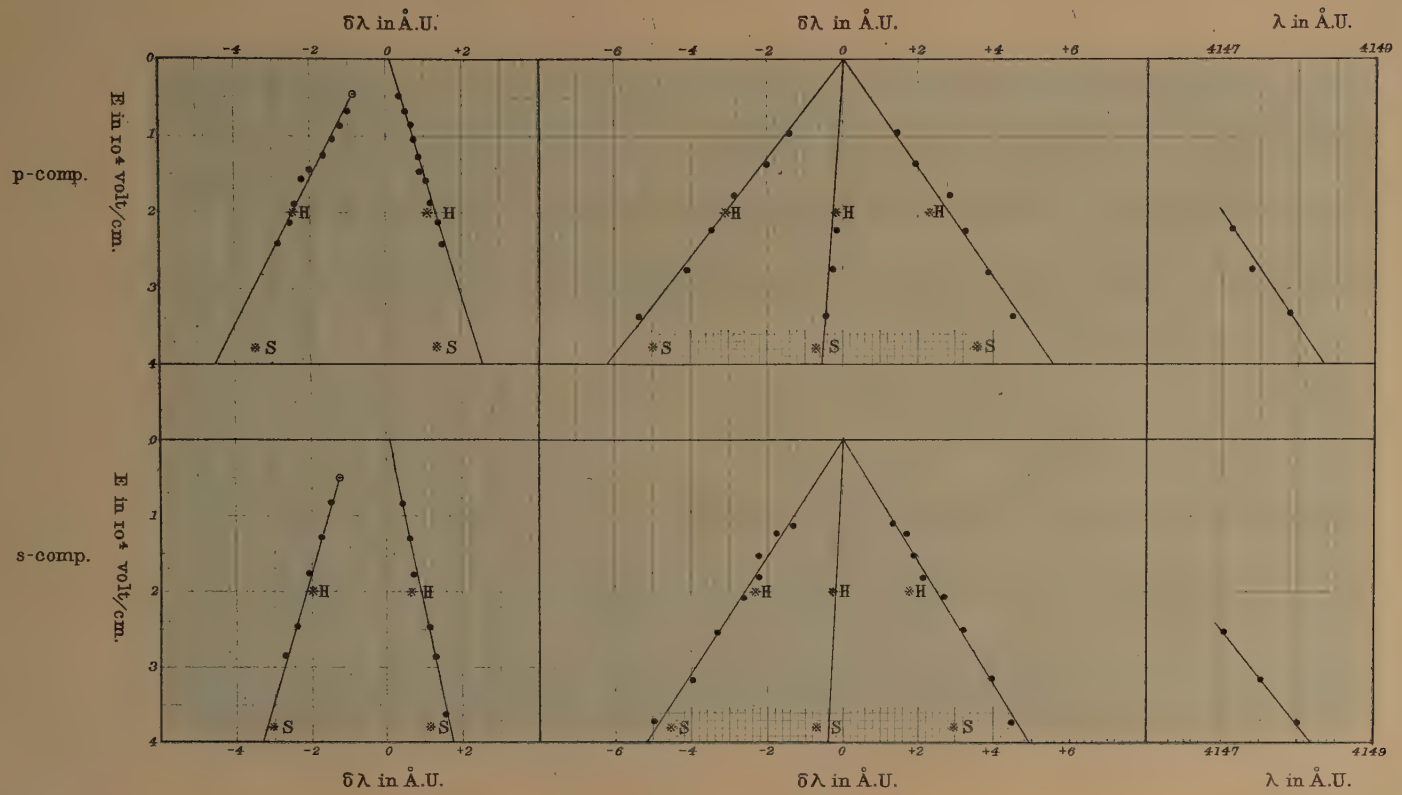


Fig. 5. λ: 4602

Fig. 6. λ: 4132

Fig. 7. λ: 4148



The Effect of an Electric Field on the Spectrum Lines of Calcium and Magnesium.

By

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(Received Feb. 23, 1918.)

§ 1.

For elementary gases, such as hydrogen and helium, the effect of an electric field on their spectrum lines has been frequently studied; and fairly concordant results have been obtained by different investigators.

On the other hand, similar researches with respect to the metallic spectra are rather few in number, and the results show many discrepancies, according to different authors.

In 1914, Stark and Kirschbaum[1] examined the transverse electric effect on the lines of *Li*, *Hg*, *Al*, *C*, *Ca*, *Mg*, *Na* and *Tl* using canal rays as the source of light. Later, a similar research was carried out by Lüssem[2] for *Li*; and also by Wendt and Wetzel,[3] for *Al* and *Hg*.

Adopting the method due to Lo Surdo,[4] Howell[5] observed both the transverse and longitudinal effect on certain lines of calcium and lithium. In Howell's experiment, no electric effect was observed for the lines of *Fe*, *Ni*, *Mg*, *Al*, *Zn* and *Sr*.

Quite recently, Anderson[6] examined the electric effect on the lines of several different metals by modifying the method of Lo Surdo. But the results are not yet fully published, except for chromium.

In the present experiment, the discharge tube used as the source of light was of Lo Surdo's type. The experimental arrangements were quite the same as reported in our former communication relating

1 Stark and Kirschbaum, Ann. d. Phys., **43**, 1017 (1914).
2 Lüssem, Ann. d. Phys., **49**, 865 (1916).
3 Wendt and Wetzel, Ann. d. Phys., **50**, 419 (1917).
4 Lo Surdo, Rendiconti d. Lincei, **22**, 664 (1913).
5 Howell, Astrophys. J., **44**, 381 (1916).
6 Anderson, Astrophys. J., **46**, 104 (1917); Phys. Rev., **9**, 575 (1917).

to the electric effect on helium lines. The metallic rod of calcium and magnesium was used directly as the cathode, the residual gas in the tube being air in most cases. In order to attain a very strong electric fields, thick-walled capillary tubes having the inner diameter of 1 or 2 mm., and the outer diameter of 5 or 6 mm. were found most suited for the purpose.

To determine the intensity of the electric field, Stark's data for H_γ line were relied on as in the case of our former experiment.

The dispersion of the three spectrographs employed in the present experiment was as follows:—

4 prism spectrograph.....	23.9 Å per mm. at	H_γ,
3 „ „	40 Å per mm. at	H_δ,
Quartz spectrograph	16 Å per mm. at	λ3000 Å,
	9 Å per mm. at	λ2500 Å.

The region examined in the present experiment ranges between λ 5100 and 2200 Å.

In Pl. III and IV, several photographs obtained by the writers are reproduced, notations // and $\perp$ being employed to represent parallel and perpendicular component respectively.

§ 2.

Calcium Lines.

Of calcium lines, Stark and Kirschbaum observed only very small displacements on the following 10 lines in a field of 44000 volt/cm. 4226 (g), 3969 (H), 3934 (K), 3737, 3706, 3179, 3159, 3645, 3631, 3624.

Here it is to be mentioned that the above authors remark that their measurements are far more inaccurate in the case of metallic spectra than in the case of helium and hydrogen lines. In fact, of the 10 lines mentioned above, the displacements were measured only for the parallel components of the four lines λ 3737, 3706, 3179, 3159. For the remaining 6 lines, we have only qualitative data as regards the sign and amount of displacement. Stark and Kirschbaum also noted that the calcium lines λ 4456, 4455, 4436, 4435 and 4426 were unaffected by the electric field.

Howell's experiments on calcium lines relate only to H and K lines. In the transverse electric effect on these two lines, one positive and one negative component was observed both for the parallel and perpendicular component.

The results obtained by the present experiment are by no means satisfactory. For most of the calcium and magnesium lines, only qualitative observations are recorded with respect to the sign of displacement in an electric field.

In order to give a glance at results, we give here a table of the affected lines of calcium grouped according to their series relations.

TABLE I.

Calcium Lines.

	I.N.S.	SL_2	Narrow triplet	Non-series line
$m=5$	*3644.5 (−)	5041.9 (+)	4586.1 (+)	*4685.4 (−)
	*3630.9 (−)	4527.2 (+)	4581.7 (+)	
	3624.2 (−)		4578.8 (+)	
		SL_3	*4098.8 (+)	
			* 95.3 (+)	
		4878.3 (+)	* 92.9 (+)	
		*4355.4 (+)		

In the above table, the lines marked by asterisks were those whose amounts of displacement have been measured. The displacements of the remaining lines were only qualitatively observed. The signs (+) and (−) refer to the side toward which the line is displaced in an electric field. SL_1, SL_2 and SL_3 are the single line series observed by Saunders[1].

In the following, detailed accounts are given for the measured lines.

(1) 3645, 3631, 3624 (Pl. I, Figs 3, 4)

In the arc spectrum, the first two lines are each a doublet; and, according to Exner and Haschek[2], we have 3644.90 (intensity 8) 3644.50 (20) and 3631.07 (8) 3630.87 (20). The lines were also studied by Crew and Mccauly[3], who used the calcium arc under re-

1 Saunders, Astrophys. J., **32**, 153 (1910).

2 Exner and Haschek, Tabellen der Bogenspectra, Wien (1904).

3 Crew and Mccauly, Astrophys. J., **39**, 29 (1913).

duced pressure as the source of light. According to them, the line 3644 consists of three lines which are resolved only at low pressure.

The dispersion of our instrument was of course insufficient to resolve these fine lines, and, as shown in Table I, we could measure only the first two lines.

Contrary to our observation, Stark and Kirschbaum record that these lines are slightly displaced toward the red side in electric field. We think it may be possible that the presence of neighbouring lines on the red side may disturb the appearance of the lines under consideration. In order to decide the question, it will be necessary to re-examine the phenomenon with greater dispersion.

(2) 4355 (Pl. I, Fig. 2.)

It is rather curious that this line, which is most distinctly affected by the electric field, has not been noted by former investigators. The mode of its displacement in two different stages of electric field ($E_{max.} = 39000$ volt/cm. and $E_{max.} = 68000$ volt/cm.) is shown in Pl. III, Figs 11*a* and 11*b*.

In Pl. I, Fig. 2, the curve showing the displacement of the parallel component is turned slightly concave upwards; but, as our measurement is by no means accurate owing to the hazy appearance of the line, the question of proportionality between the field strength and the amount of displacement cannot be definitely settled by the present experiment.

(3) 4099, 4095, 4093 (Pl. I, Figs 5, 6, 7)

In 1905, Fowler[1] observed a new triplet series in the strontium spectrum, in which the lines are situated more closely together than in the Rydberg triplet, and denoted the new series as "narrow triplet." Similar series of lines were subsequently found by Saunders[2] in the calcium spectrum.

In the present experiment, the electric effect on the first member λ 4586, 4582, 4579, corresponding to $n=3$ in Saunder's notations, was

1 Fowler, Astrophys. J., **21**, 181 (1905).

2 Saunders, Astrophys. J., **21**, 195 (1905).

only qualitatively observed, while the next member under discussion appeared fairly well in the neighbourhood of $H\delta$. In the reproduction Pl. III, Fig. 12, the components of $H\delta$ appear only very faintly.

Unfortunately, the initial position of the line λ 4093 is obscured by an impurity line.

As shown in the diagrams, Pl. I, Figs. 5, 6, 7, all the members of this triplet are affected in nearly the same manner. A similar feature was observed for the magnesium triplet 3097, 3093, 3091 also.

It is important to remember that the phenomenon of the Zeeman effect gives great facility for discriminating the series relation in spectrum lines. Quite analogously, we may expect that the effect of an electric field also will furnish us another powerful means for discriminating the series relations. For such a purpose, systematic studies on the electric effect for lines having well known series relations seem to be of much importance.

We may even proceed a step further and remark that for some particular class of lines, for instance, the narrow triplet lines of calcium above described, the electric effect is perhaps more easily observed than the Zeeman effect, since these lines are intensely excited only in a strong electric field.

It may worthy of note that most of the affected lines above described are denoted as "hazy" in the wave-length tables given by Saunders[1] for the arc spectrum of calcium. Thus, in his table the lines 5042 (+), 4878 (+), 4355 (+), 4099 (+), 4095 (+), 4093 (+) are marked hR (hazy toward the red), while the line 4685 (−) is marked hV (hazy toward the violet). The broadening of the narrow triplet lines 4099, 4095, 4093 toward the red side was noted by Crew and Mccauly[2] also in the calcium arc spectrum under reduced pressure.

An exceptional case occurs for the triplet 3645, 3631, 3624, marked hR in Saunder's table, but displaced toward the violet in electric field.

(4) Enhanced lines of calcium.

With the dispersion used in the present experiment, no marked effect was presented by the enhanced lines of calcium up to the field of 90000 volt/cm.

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1 Saunders, loc. cit.

2 Crew and Mccauly, loc. cit.

For H and K lines, we could only observe that they were considerably broadened in strong field, notably toward the violet side. In the transverse effect of these lines at $E=20000$ volt/cm., Howell observed a separation of about 1 Ångström for both of the p- and s-components. We were unable to observe such a large separation, and it appears that our observation is more in conformity with that of Stark and Kirschbaum.

According to Stark and Kirschbaum, the next member 3737, 3706 as well as lines 3179, 3159 and the strong arc line 4226 (g) are said to be displaced toward the red; but we were unable to observe the phenomena.

In agreement with Stark and Kirschbaum, the following calcium lines were found to be unaffected by electric field:

4318.8, 4307.9, 4302.7, 4299.1, 4289.5, 4283.2

§ 3.

Magnesium lines.

In Table II, we give a list of the affected lines with their series relations:

TABLE. II.

Magnesium Lines.

	I.N.S.	S.	Non-series line
$m=4$	3838.4 (−)?	4703.3 (+)	4571.3 (−)
	32.5 (−)?	*4352.2 (+)	
	29.5 (−)?		
$m=5$	*3097.1 (+)		
	* 93.1 (+)		
	91.2		

(1) 4352 (Pl. II, Fig. 8.)

As shown in Table II the line belongs to the diffuse single line series, together with the line λ 4703. Both of these lines are displaced

toward the red side in the electric field. The photographs showing the line $\lambda 4352$ at the fields $E_{max.} = 58000$ volt/cm. and $E_{max.} = 74000$ volt/cm. are reproduced in Pl. IV, Figs. 13 *a*, 13 *b*.

(2) 3097, 3093 (Pl. II, Figs. 9, 10.)

These two lines, together with the line $\lambda 3091$, form a triplet in the first subordinate series. In our photograph, the line 3091 was obscured by an impurity line.

In Pl. IV, Fig. 14, a portion of a photograph obtained by a quartz spectrograph is reproduced.

There still remains much doubt about the behavior of the strong triplet 3838, 3833, and 3830 in the electric field. In our study, they showed a tendency of being displaced toward the violet side in a very strong field; while Stark and Kirschbaum state that a component appeared on the red side of each line. Since the dispersion of our instrument was very small (about 30 Å per mm. at these lines), the results obtained in the present experiment cannot be taken as decisive, and we hope to investigate, in the near future, the phenomenon more thoroughly by means of a plane grating.

Just as in the case of the calcium non-series line $\lambda 4686$, a magnesium non-series line 4571 was found to be displaced to the violet side in an electric field.

The well known triplet 5183, 5173, 5168 appeared with great intensity at the cathode, but no electric effect was observed for these lines. A similar remark applies to the line 2852, belonging to the first subordinate series.

(3) Enhanced lines of magnesium.

Stark and Kirschbaum observed that the enhanced lines 2803 and 2796 showed a red side component in the electric field. Although a number of enhanced lines appeared in our photographs, we were unable to detect the electric effect on these lines.

It may be noted that the line 4481 always appeared with great intensity, while the line 3105 was very weak. The lines 2936, 2929, 2803, 2798, 2796 and 2791, belonging to the wide doublet series in the classification of Fowler[1], appeared with considerable intensities.

1 Fowler, Phil. Trans., A. **214**, 225 (1914).

In connection with this, it may be remarked that in some of our photographs mercury lines appeared as impurity lines. According to Stark and Kirschbaum, the following 10 mercury lines are all displaced slightly toward the red side in an electric field :—

4359, 4078, 4047, 3663, 3655, 3650, 3132, 3131, 3126, 3022.

In our case, we could find no sign of the said effect on these lines even though the dispersion of our instrument was sufficiently great for detecting it.

§ 4.

As remarked by Howell[1], the spectra of metals used as the cathode in the Lo Surdo tube are in many respects different from the ordinary arc and spark spectra. Further, in these cathode spectra, the relative intensities of various arc and spark lines are greatly influenced by the nature of the residual gas employed. As was remarked by Anderson[2], the metallic spectra are generally brighter in oxygen or air than in hydrogen, and, in fact, most of the affected lines of calcium and magnesium above described were more strongly developed when the residual gas was air.

In the course of measuring the photographs, we noticed that the following lines of unknown origin appear very often on the plates :—

A. 4367.1
B. 4152.8
C. 4110.7 (slightly displaced toward the violet side in electric field)
D. 4100.3 (do)

These lines appeared in all cases using *Al*, *Ca*, *Mg*, and *Ta** as the cathode, the residual gas being air or hydrogen. They were especially strong near the cathode, and some of them were evidently displaced by the electric field in the direction above indicated. As our photographs show many impurity lines, beside the bands of *N* and *CO*, we cannot be sure of anything as regards their origin. So

1 Howell, loc. cit.

2 Anderson, loc. cit.

* It may worthy of note that, in the case of tantalum cathode, the disintegration is considerably smaller than that of aluminium.

far, our search for the likely corresponding lines in the wave-length tables of the cathode metals has all been in vain. In Howell's paper, it is stated that three new lines were found in the case of *Mg* cathode. These lines are nearly coincident with *B*, *C* and *D* in the above table, but we think it very unlikely that the lines found in the present case are due to *Mg*. Some of these lines are marked in the reproductions shown in Pl. III and IV.

Summary.

1. Employing Lo Surdo's method, the effect of an electric field on the following *Ca* and *Mg* lines has been investigated :—

Ca : 5042, 4878, 4685*, 4586, 4582, 4579, 4527, 4355*, 4099*, 4095*, 4093*, 3645*, 3631*, 3624.

Mg : 4703, 4571, 4352*, 3097*, 3093*.

On the lines marked by asterisks, quantitative measurements have been carried out. The maximum electric field employed was about 90000 volt/cm.

2. All the above lines were displaced either toward the red or toward the violet in the electric field.

3. In general, the lines belonging to the same series were affected in nearly the same way, and further, each line constituting a triplet was affected in a similar manner. The latter statement is well exemplified in the case of the calcium lines 4099, 4095, 4093 belonging to the "narrow triplet" series.

4. An exceptional case seems to be the magnesium triplet λ 3838, 3833, 3830; but, as the lines are only very slightly affected, further experiments, using a larger dispersion, are needed for ascertaining the phenomenon.

In conclusion, we wish to express our sincere thanks to Prof. T. Mizuno for the interest he has taken in the work.

Fig. 1. λ: 4685 4 Fig. 2. λ: 4355.4 Fig. 3. λ: 3644.5 Fig. 4. λ: 3630.9

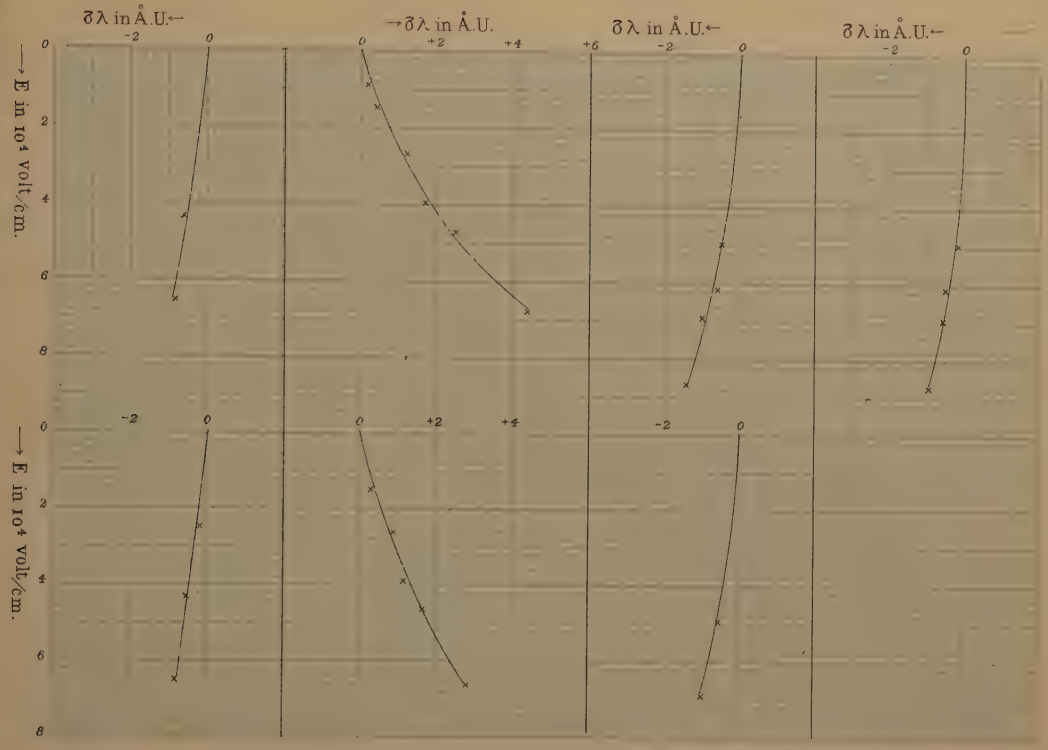
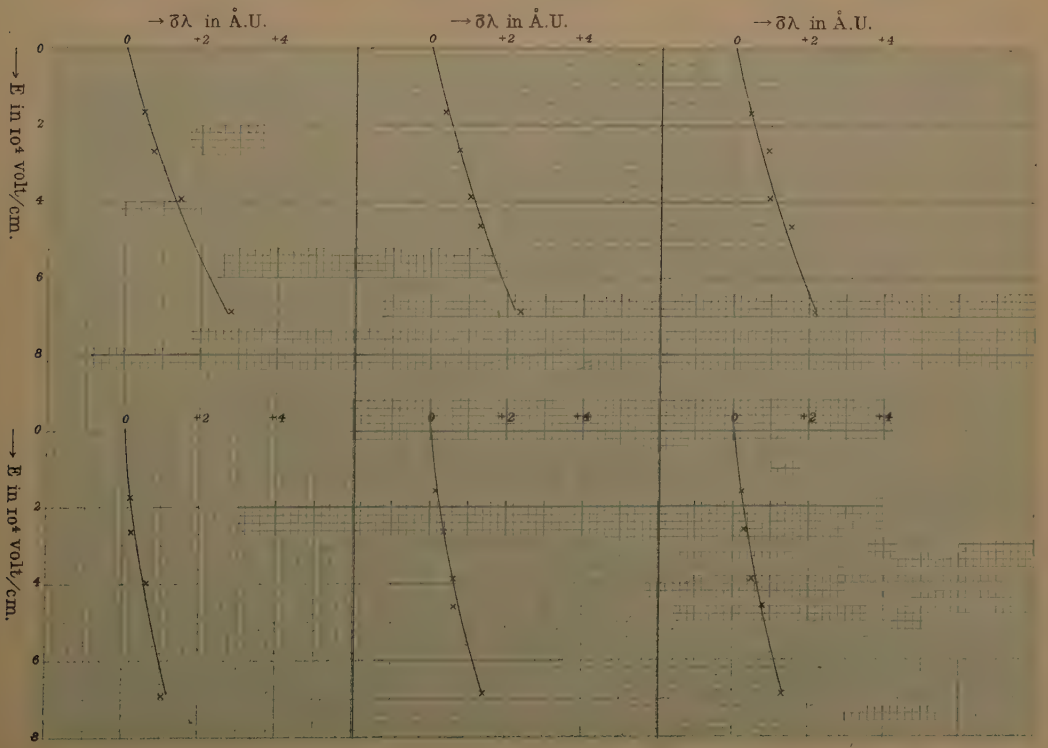


Fig. 5. λ: 4098.8 Fig. 6. λ: 4095.3 Fig. 7. λ: 4092.9



Magnesium.

Fig. 8. λ: 4352.2 Fig. 9. λ: 3097.1 Fig. 10. λ: 3093.1

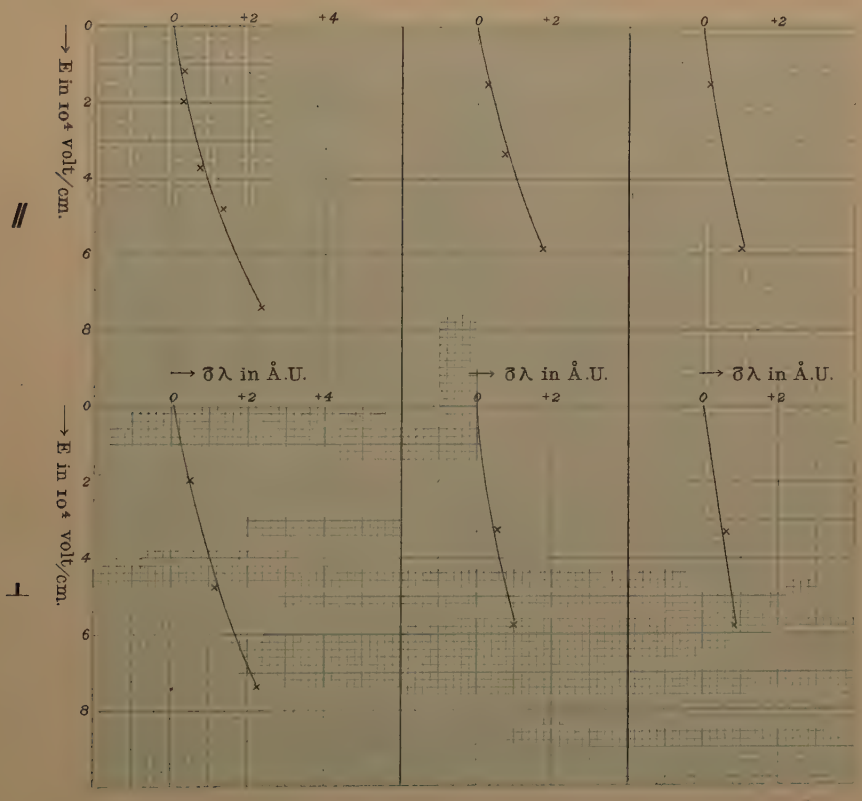


Fig. 11a. Ca λ : 4355

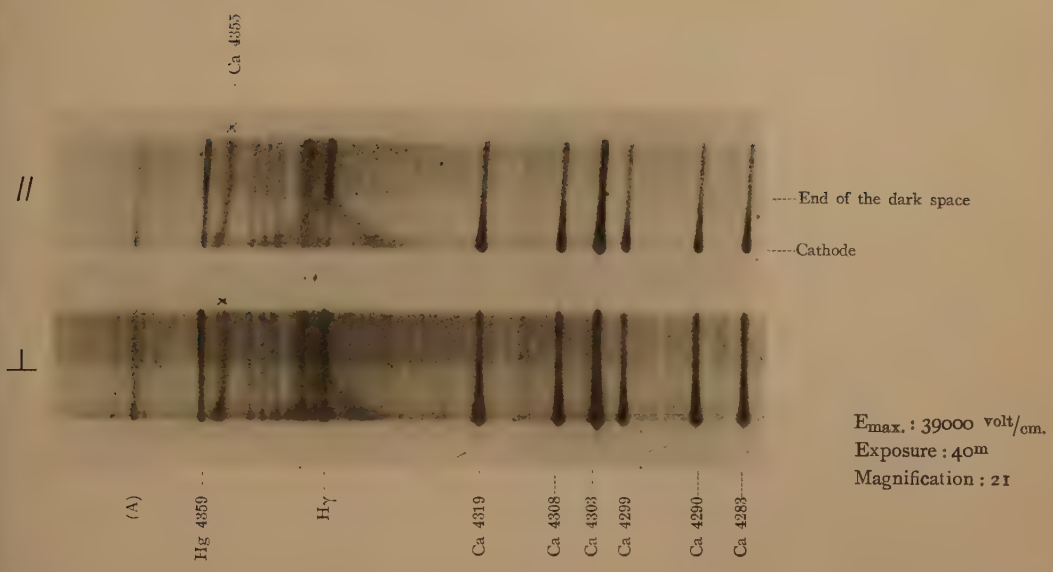


Fig. 11b. Ca. λ : 4355

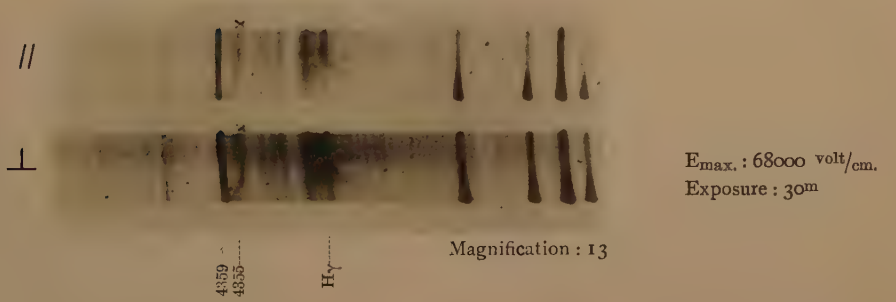


Fig. 12. Ca (λ : 4099, λ : 4095, λ : 4093)

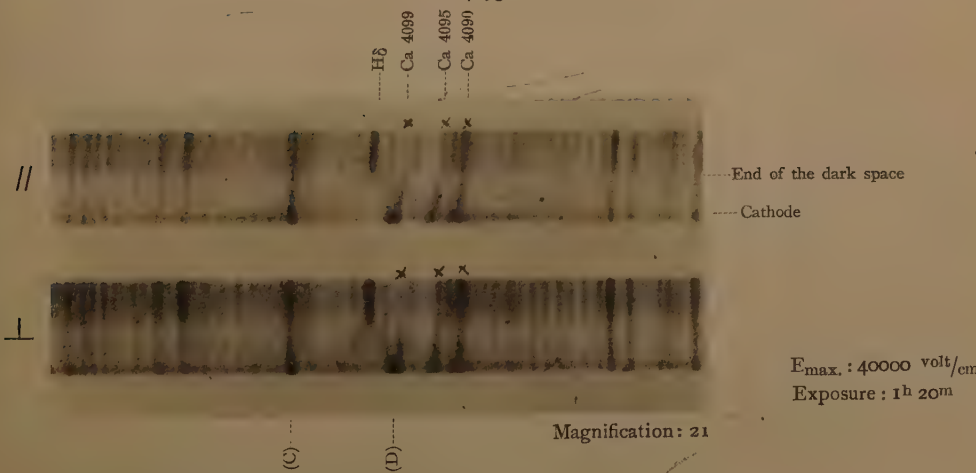
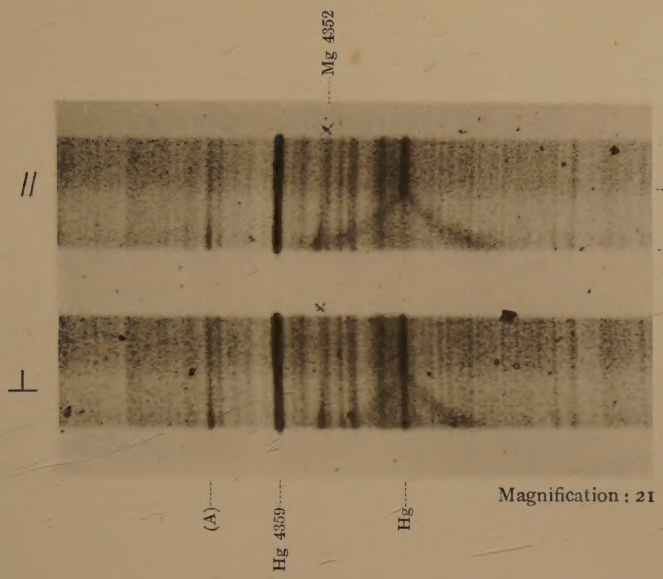


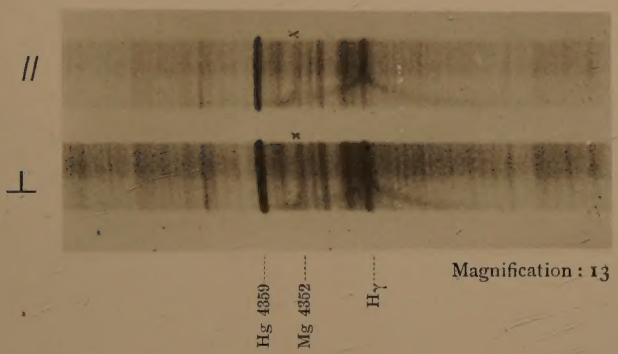
Fig. 13a. Mg λ : 4352



$E_{max.}$: 58000 volt/cm.
Exposure : 40m

Magnification : 21

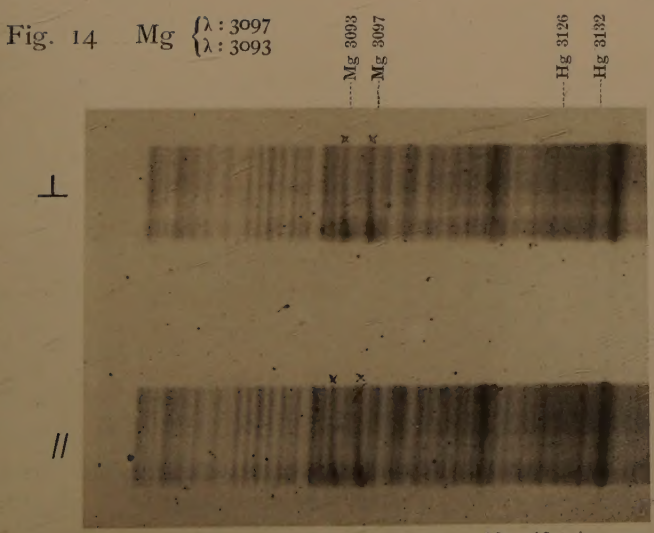
Fig. 13b. Mg λ : 4352



$E_{max.}$: 74000 volt/cm.
Exposure : 40m

Magnification : 13

Fig. 14 Mg $\begin{cases}\lambda : 3097 \\ \lambda : 3093\end{cases}$



$E_{max.}$: 58000 volt/cm.
Exposure : 40m
Quartz spectrograph

Magnification : 15

Vol. III., No. 6, Published June 20th, 1918.

Price - - - Yen 0.70

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO, FUKUOKA & SENDAI.

大正七年六月十七日印刷

大正七年六月二十日發行

編纂兼發行者　京都帝國大學理科大學

印刷者　大久保秀次郎

東京府北豐島郡巢鴨町三丁目十番地

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